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Accelerated Weathering: Development of Fail/Pass Requirements for Low VOC Alkyd Enamels

by Kestutis G. Chesonis

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TT-E-489, a high-gloss alkyd enamel, was reformulated to be lead and chromate free and meet the maximum 3.5 lbs/gal Volatile Organic Compound (VOC) EPA requirement. This report describes the evaluation of various ultraviolet light sources as used for accelerated weathering testing. Fail/pass criteria were the resistance to color change and to loss of gloss.			
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1. Introduction

1.1 Background Information

Due to the Clean Air Act of 1977 and decisions by the Department of Defense, specification TT-E-489 High Gloss Enamel was reformulated to meet the 420 g/l (3.5 lbs/gal) maximum content of Volatile Organic Compounds (VOC) as stated in the Federal EPA Control Techniques Guideline (CTG) limit for Miscellaneous Metal Parts and Products. Pigmentation had to be lead- and chromate-free to eliminate exposure and hazardous waste generation. In meeting VOC restrictions, reformulation is the most cost-effective method since it minimizes changes in the application and curing equipment and eliminates the need for expensive pollution abatement equipment.

The Organic Chemical Coatings Group (OCC) of the Materials, Fuels and Lubricants Directorate, US Army Belvoir RD&E Center (BRDEC) was the preparing activity for TT-E-489 Enamel, a Qualified Products List (QPL) coating.¹ It is a high-quality, air-drying enamel purchased in high volumes by General Services Administration (GSA) for use on various surfaces. Previously, TT-E-489 was manufactured using medium oil-length alkyds defined by TT-R-266 Type III. Many companies made these alkyd resins and formulating parameters such as types and amounts of driers, additives and solvents were widely known. To meet the 3.5 lbs/gal VOC requirement, resin manufacturers had to develop new alkyds at lower molecular weights and viscosities so that lesser amounts of solvent would be used to obtain a sprayable end product, a high solids, low VOC enamel.

1.2 Objectives

In reformulating TT-E-489, the OCC group set the following goals:

- a. To retain the same maximum drying times of 2 hours and 8 hours for set-to-touch and dry hard.
- b. To define a strict viscosity reduction prior to application. This would ensure an acceptable sprayable product at a known VOC content.

¹ Currently part of Army Research Laboratory, Materials Directorate.

c. To develop a fast, reproducible, industry-wide accelerated weathering test to screen acceptable from non-acceptable alkyd resins and their formulations without the waiting period necessary for natural outdoor exposure.

Prior to the appearance of high solid alkyds, the variables for a given alkyd type were defined by price changes of the oil and polyol from which it was made. The need to maintain a specified quality resulted in a rather narrow window for raw material experimentation and resulted in resins that were low-cost, easy to manufacture and predictable in quality. The demand for lower viscosity, high solids alkyds to make low VOC coatings resulted in a dramatic opening of the formulation window for new raw materials and techniques. Alkyd formulas became proprietary and their ability to match the old standards for drying time and outdoor durability had to be critically evaluated. One of the major ways to evaluate a high solids alkyd resins was in finished coating in an accelerated weathering cycle to see how well they maintained their gloss properties and resistance to color change.

How the data base for goal c was collected and utilized is the subject of this Technical Report. It should be noted that the purpose of these evaluations was to show the feasibility of meeting the specification requirements and not a rigorous comparison of resins and pigments, nor the fine tuning of a formula to lower the cost and still meet all of the requirements.

2. Experimental

2.1 Procedures

In requiring a coating to pass accelerated weathering, two separate entities are actually evaluated: the polymer resin itself and the formulated coating. While it is impossible to make a good coating from an inferior resin, it is quite simple to make a bad coating from a quality resin. In formulating alkyd enamels, the choice of metal driers (catalysts) is of paramount importance. Without them, films would stay soft for weeks and would be susceptible to damage from exposure and moisture. Thus, accelerated weathering is used to ensure that the actual coating will not lose its high gloss or change color when exposed to sunlight and moisture.

Eighteen resin samples from nine manufacturers were evaluated in standardized formulas using the recommended drier combination from the suppliers. Only three resins from different manufacturers met the stated goals. Most failed to meet the dry times or the VOC requirement. Observations during the early screening tests indicated the need to add requirements for print resistance and resistance to wrinkling in heavier films.

2.2 Apparatus

The requirements of TT-E-489G prior to revision stated that for accelerated weathering, ASTM Method G-23 (Carbon Arc) be run for 168 hours. After exposure, the panels had to have a gloss loss of less than 30% and a color change less than four units as defined in the specification.

In developing an improved accelerated weathering test, emphasis was placed on finding a method that was low-cost, required minimum maintenance and gave reproducible results. In this study, panels were exposed to accelerated weathering using ASTM Method G-53 Fluorescent UV-Condensation and ASTM Method G-26 Xenon Arc. In ASTM Method G-53, two different lamps were evaluated, UVB-313 and UVA-351. The main difference between these lamps is that the UVB-313 emits in the 280-300nm range, irradiance not present in natural sunlight whereas UVA-351 emittance is similar to sunlight through a glass. After this study was initiated, a new lamp, UVA-340, was introduced whose emittance is very close to that of sunlight. These results were compared to panels exposed to natural weathering for two years at Fort Belvoir, VA.

2.3 Panel Preparation

The old requirement for an 8:1 reduction with a thinner for spray application was kept. After evaluating various formulas with conventional and High Volume Low Pressure (HVLP) spray guns, a maximum 70 KU viscosity after the 8:1 thinner reduction was specified. The package viscosity was not controlled, but the reduced enamel had this maximum viscosity cap and the VOC content was measured after reduction. This allowed leeway in formulating and still kept the playing field level. Dry films of 1.4-1.6 mils on aluminum 4X12 inch panels (A412, Q Panel Co.) were air dried for seven days prior to exposure.

2.4 Drying Times (Before Exposure)

Seven formulas using five different high solid alkyds were air dried for three and seven days prior to exposure to study the effect of this variable on performance. No differences were noted on exposure to the Xenon Arc, but all the three day air dried panels exposed to the fluorescent UV showed various degrees of water spotting and streak marks. Panels air dried for seven days did not show this defect.

3. Results and Discussions

3.1 Tests Performed

Initial accelerated weathering was performed on six non-high solid samples on hand from various manufacturers to evaluate panel preparation, apparatus variables and data. Light sources were 6000W for the Xenon Arc and UVB-313 and UVA-351 for the fluorescent with an eight hour light cycle at 60°C followed by four hour condensation at 50°C. Figure 1 shows the results of a 200 hour exposure to the three systems. Gloss reduction showed a typical pattern and color change in CIELAB units showed minimal change for the black, grey, and red samples. The yellow made with lead chromate pigments showed noticeable darkening and both whites had a change of 1.9-2.1 units for the UVB-313 and 0.7-0.9 units for the UVA-351.

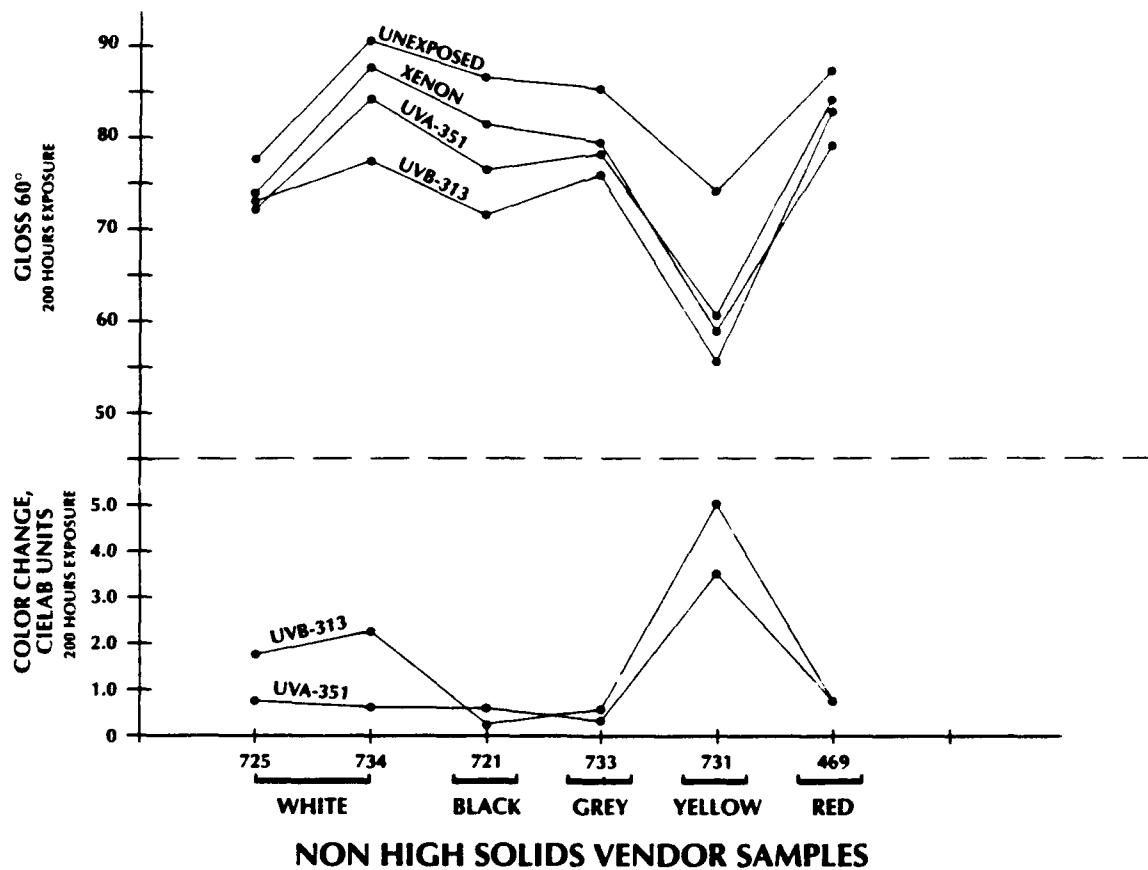


Figure 1. Gloss and Color Change After Exposure

The initial evaluation of high solid resins in a series of gloss white enamels was made based on this formula:

RCI resin @ 85% T.S.	-	200g
Mineral Spirits	-	30g
Nuosperse 700	-	4g
10% Calcium	-	4g
SD-2	-	4g
T ₁ O ₂	-	259g

Dispersed on high speed mixer to a 7 1/2 F.G., then added:

Resin @ 85% T.S.	-	235g
Mineral Spirits	-	90g
MIBK	-	70g
12% Cobalt	-	2g
24% Zirconium	-	4g
Active 8	-	1g
Anti-Skinning Agent	-	<u>2g</u>
		<u>905g</u>

Viscosity = 69 KU (after 24 hours)

Pigment to Vehicle Ratio = 0.7:1.0

Total Non-Volatile = 71.0

Wt/Gal = 10.17

VOC = 2.95

Other colors were made by changing the pigment-to-vehicle ratio to meet the minimum values for hiding power and using solvent amounts to keep the VOC below 3.5 lbs/gal at a maximum viscosity of 70 KU. Adjustments for resin solids and driers were made as required. The type of solvents used was not as critical as the evaporation rate. The use of excess top driers such as cobalt with fast solvents caused an early surface-dry that actually inhibited dry through and resulted in failures at the eight hour dry hard film check.

To meet the weather resistance requirement, panels exposed at Fort Belvoir for two years had to have only moderate chalking and the color had to remain a general match. For this reason, the specification allowed only the following pigments:

Table 1. Allowed Pigmentation

PIGMENT	COLOR INDEX NAME	COLOR INDEX NUMBER
Titanium dioxide white	PW6	77891
Carbon black	PBk7	77266
Iron oxide black	PBk11	77499
Iron blue	PB27	77510
Phthalocyanine blue	PB15	74160
Phthalocyanine green	PG36	74265
Arylide yellow	PY74	11741
Arylide yellow	PY65	11740
Diarylide yellow	PY83	21108
Iron oxide yellow	PY42	77492
DNA orange	PO5	12075
Pyrazolone orange	PO34	21115
Benzimidazolone orange	PO36	11780
Naphthol red	PR170	12475
Quinacridone red	PR202	73905
Quinacridone red	PR122	73915
Quinacridone violet	PV19	46500
Iron oxide red	PR101	77491
Iron oxide brown	PBr6	77491, 77492, 77499
Iron oxide brown	PBr11	77495

3.2 Results

3.2.1 Gloss Change After Accelerated Weathering. Eighteen formulas, non-chromate and non-lead and meeting the 3.5 lbs/gal VOC requirement at application, were exposed for 200 hours using UVA and UVB lamps. Results are shown in Figure 2. Weathering depends on a synergistic relationship between polymers and pigments in that the light fastness of a pigment can dramatically effect the values of a given resin.

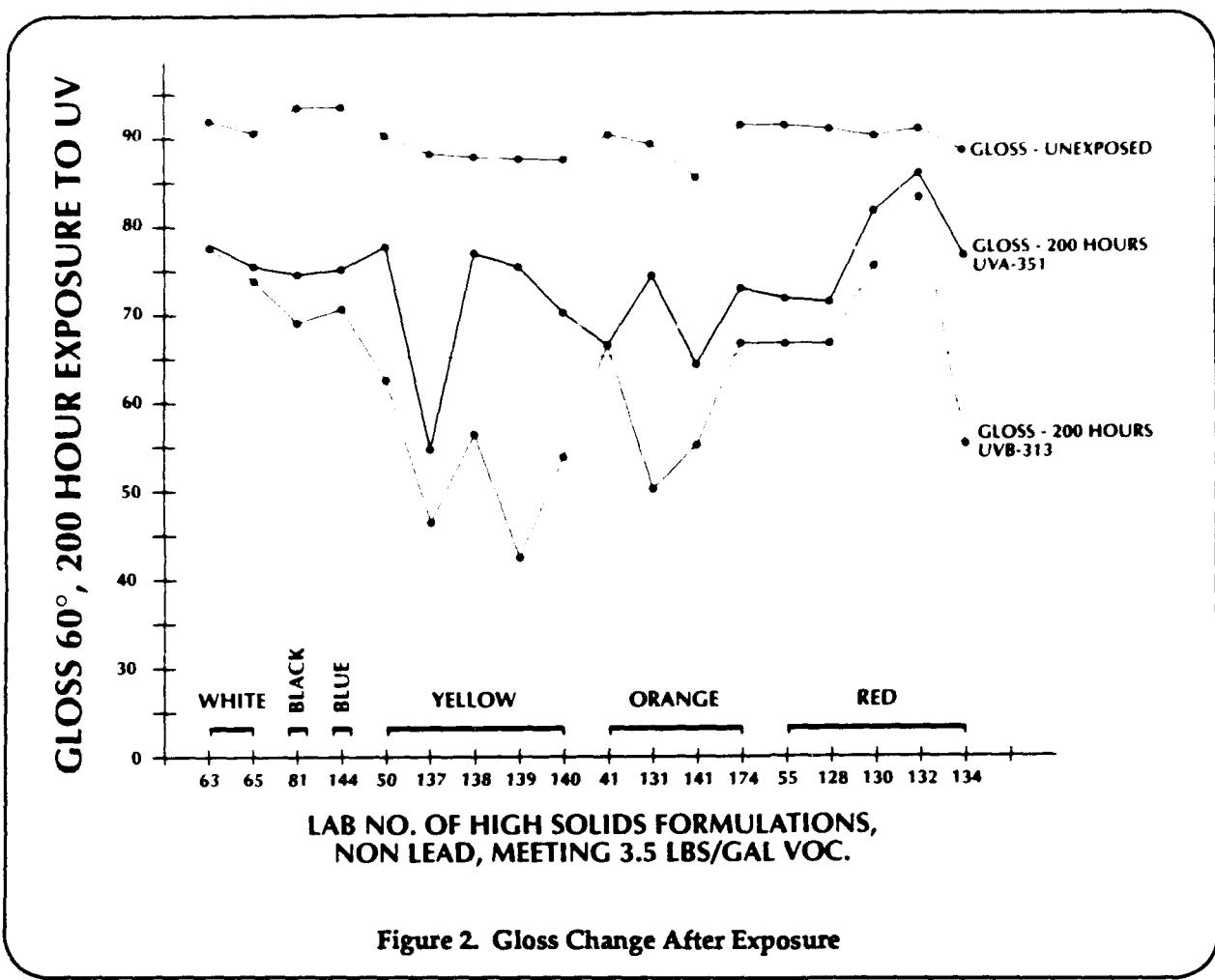


Figure 2. Gloss Change After Exposure

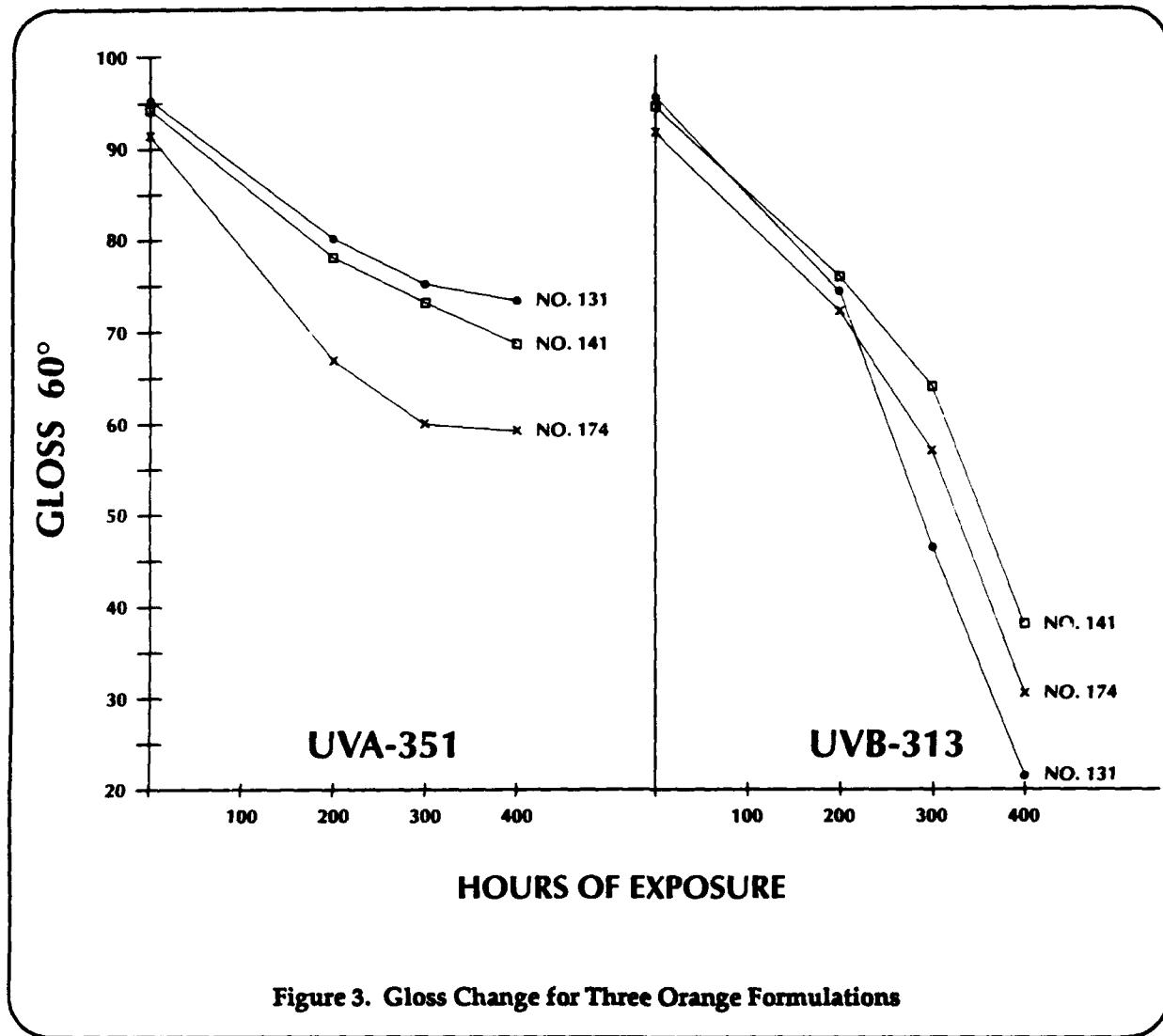
Pigmentation of formulas in Figure 2 is as follows:

Formula No. 63 - PW6, Resin A, 0.7:1.0 Pigment: Vehicle Ratio

- 65 - PW6, Resin B
- 81 - PBK7, Resin A
- 144 - PB27 & PB15, Resin A
- 50 - PY83, Resin C
- 137 - PY65, Resin A
- 138 - PY74 & PY65, Resin A
- 139 - PY74 & PO36, Resin B
- 140 - PY74 & PO5, Resin C
- 41 - PO34, Resin C, has Barium Sulfate as Extender
- 131 - PO36, Resin B
- 141 - PO5, Resin A
- 174 - PO34, Resin B
- 55 - PR170, Resin A
- 128 - PR48:4 & PO5, Resin B
- 130 - PR48:4 & PO34, Resin A
- 132 - PR170, Resin C
- 134 - PR122 & PO5, Resin C

Figure 2 showed that a 200 hour exposure to UVA-351 failed one and marginalized two formulas using 65 gloss as the minimum. The UVB-313 had a more severe effect on most of the formulas with two (138 and 131) showing a pronounced lowering of the gloss and one (41) showing a reverse effect.

Exposures were repeated on three orange formulations made with different pigmentation to study the effects of exposure up to 400 hours. Figure 3 shows the gradual loss of gloss with UVA-351 and the severe deterioration with UVB-313.



3.2.2 Color Change After Accelerated Weathering. Color change was the second test evaluating pigment/resin systems under accelerated weathering. In Figure 4, chalking caused the high values for color change with flat and semifluous formulas, with UVB-313 being more severe and giving higher numbers. Using a maximum value of 2.5 CIELAB units after 200 hours of exposure to UVA-351, one formula failed and one was marginal. All of the high gloss formulas passed. Figure 5, a companion to Figure 2, showed that color change and gloss reduction did not go hand-in-hand, since some formulas passed one and failed the other and vice-versa. However, there were formulas that passed both without problems.

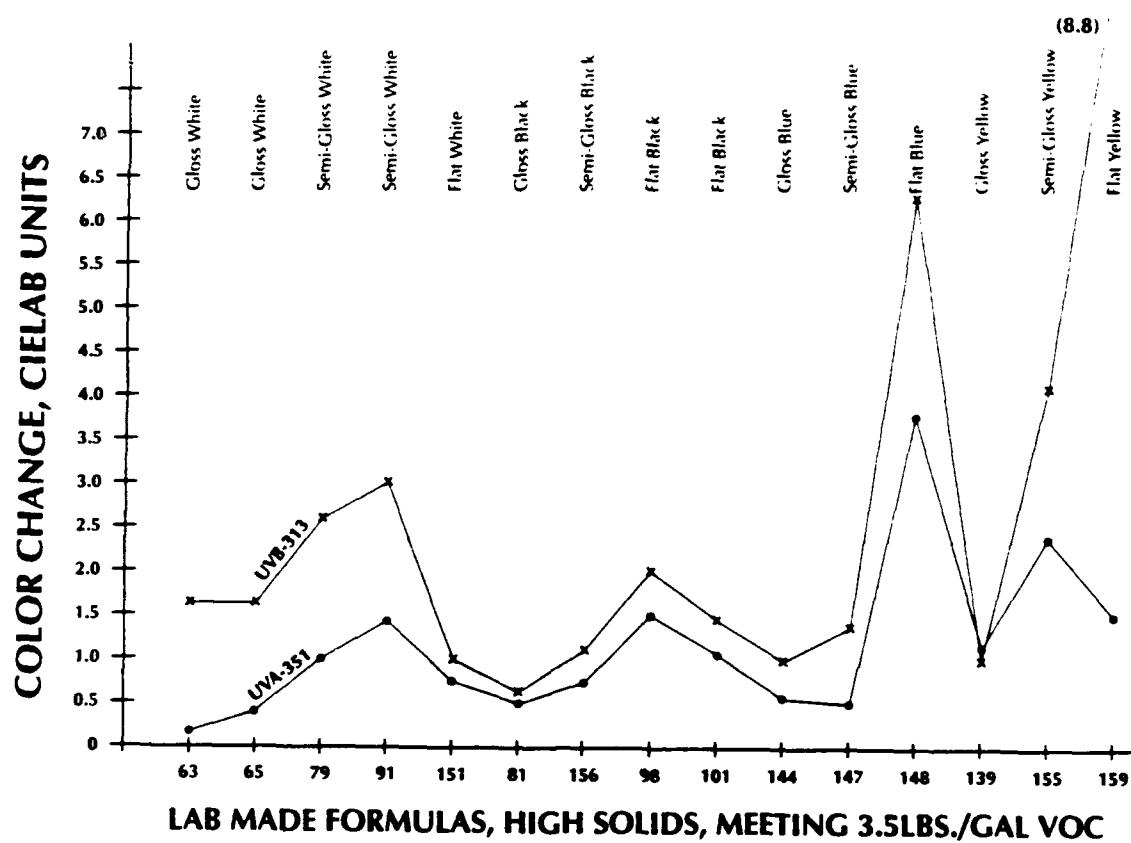


Figure 4. Color Change After Exposure

COLOR CHANGE, CIELAB UNITS

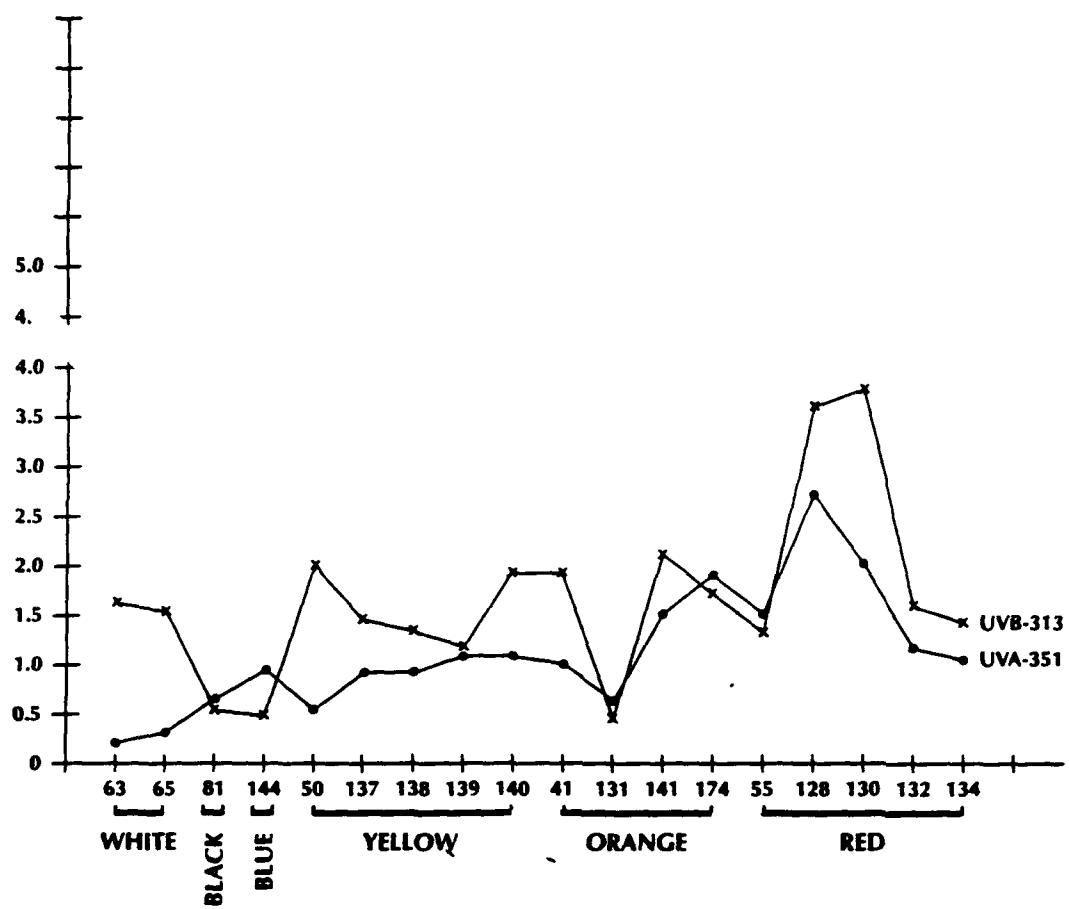


Figure 5. Color Change After Exposure

Since UVB-313 lamps emit ultraviolet rays not present in sunlight, the possibility of anomalous results was possible. To evaluate this possibility, five flat black enamels with high solid alkyd resins were compared to the old camouflage paints made with regular alkyds as per MIL-E-52798 and to the current camouflage system based on urethanes as per MIL-C-46168 and MIL-C-53039. Figure 6 shows the color change, mostly chalking, when exposed to Xenon Arc, UVA-351 and UVB-313.

The five black formulas using high solid alkyds gave expected results for all three exposures. Most of the camouflage coatings, alkyd and urethane, showed severe chalking only under UVB-313 exposure. This was in contrast to the known good weathering properties of these coatings. This data raised serious doubts on the use of UVB-313 to predict actual weathering.

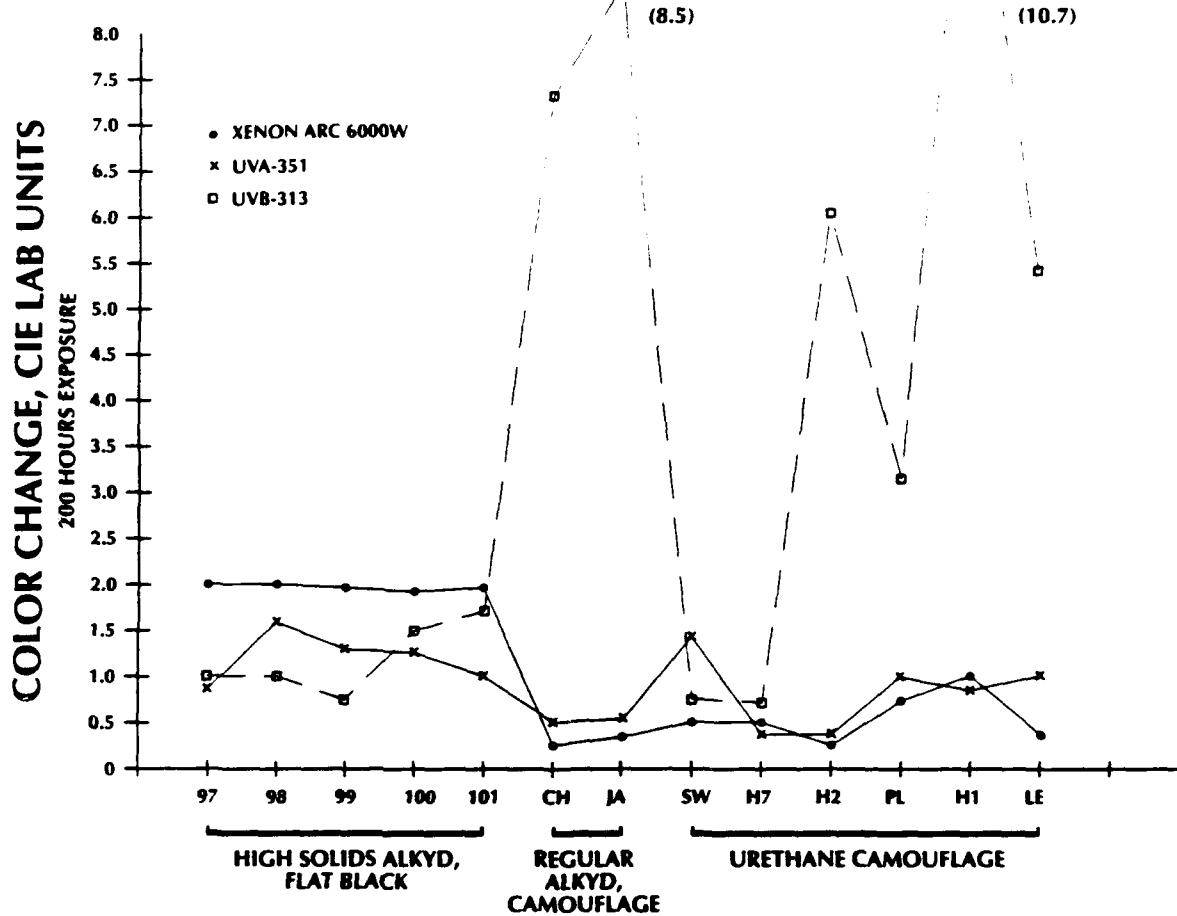


Figure 6. Color Change After Exposure

3.2.3 Outdoor Exposure at Ft. Belvoir, VA. Figures 7 and 8 show superimposed results (over Figures 2 and 5) of 24 months of outdoor exposure at Ft. Belvoir, VA. From these two charts, acceptable formulations are possible for whites and all the tinted versions, blacks, blues, and yellows using PY65 and PY74, oranges using PO34 and PO36 and reds using PR170. Formula 41 showed a severe loss of gloss attributed to the use of a short oil chain-stopped alkyd. The revised specification mandated the use of medium oil length alkyds.

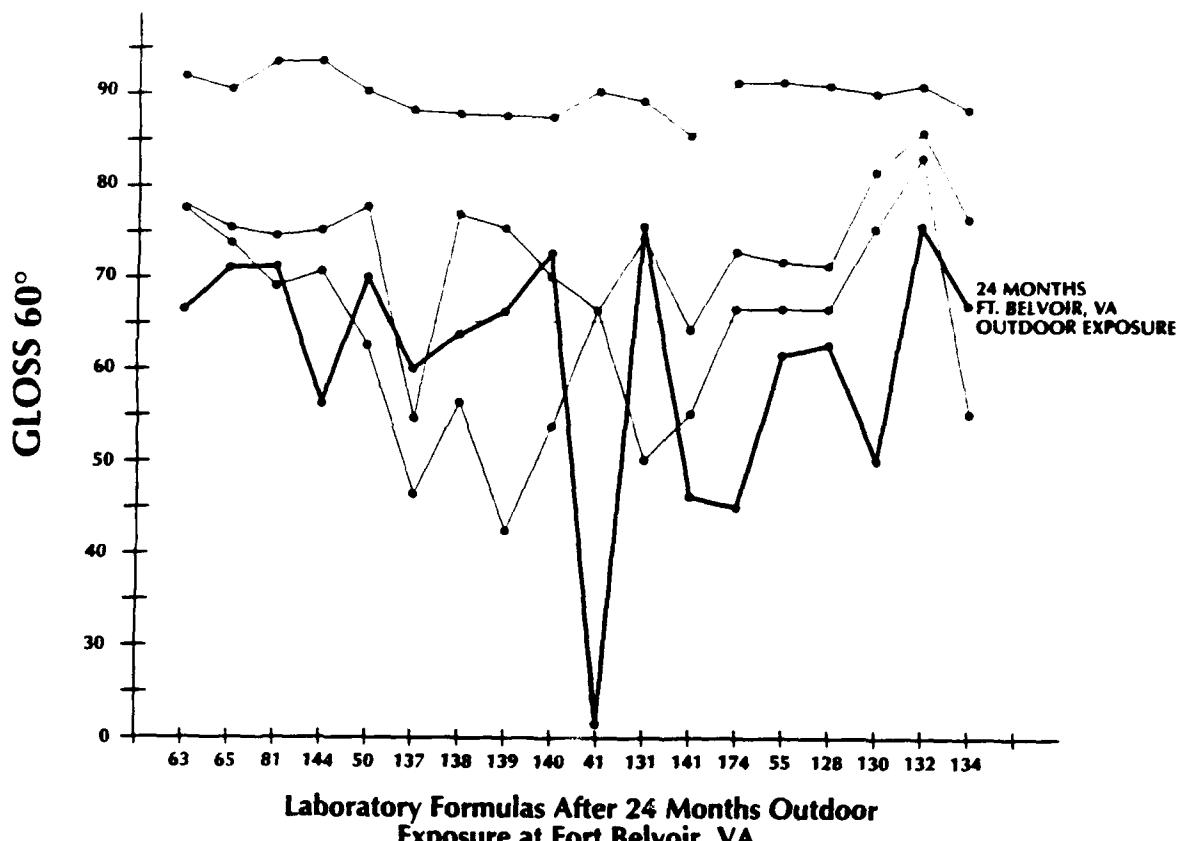


Figure 7. Gloss Change After Ft. Belvoir Outdoor Exposure

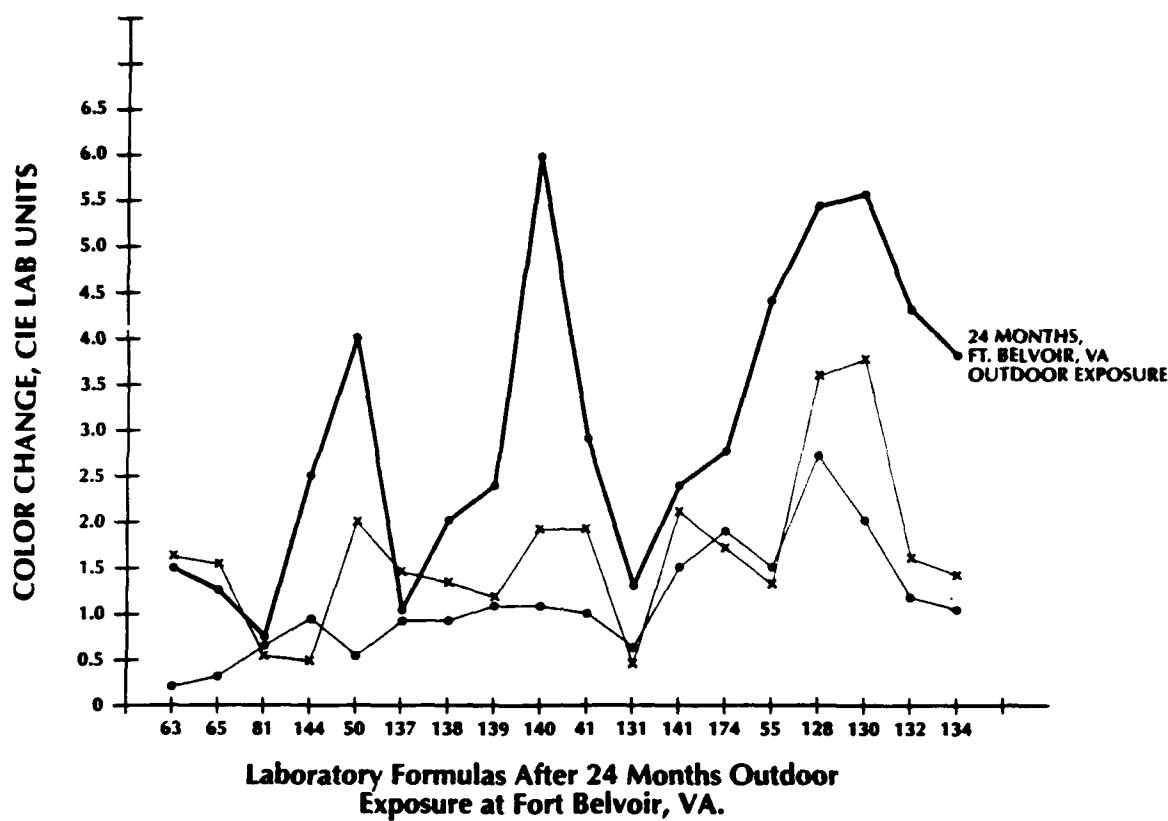


Figure 8. Color Change After Ft. Belvoir Outdoor Exposure

4. Conclusions

By comparing existing non-high solid formulations with laboratory-made high solid versions exposed to the outdoors (Ft. Belvoir, VA), Xenon Arc, UVB-313 and UVA-351, two criteria were set: one was a minimum gloss of 65 (60°) and the other a maximum color change of 2.5 CIELAB units after exposed to 200 hours of UVA-351. VOC compliant enamels can be formulated to meet these requirements; however, the reformulated TT-E-489 also states "the use of the specified pigments does not guarantee that a product will meet all of the requirements of this specification, as the choice of vendors, amounts, methods of dispersion and incorporation can significantly affect the quality of the end product". It is fair to say that the quote also applies to the alkyd resin.

Requiring a coating to maintain gloss and color stability is a highly visible element of its function that needs a synergistic blend of the pigments, polymers, and additives. With these two requirements, coatings can be evaluated in 200 hours of laboratory exposure with a fair degree of confidence in their performance in real life.

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